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<p>(54) Title: METHOD OF PROCESSING OF LIGNOCELLULOSE MATERIALS BY CONTINUOUS PRESSURE HYDROLYSIS AND CORRESPONDING EQUIPMENT</p> <p>(57) Abstract</p> <p>The invention relates to a method and an equipment for the processing of lignocellulose materials by continuous pressure hydrolysis, optionally in the presence of inorganic acid, by consequent expansion and separation of the hydrolysate and gaseous phase, wherein disintegrated raw material is wetted (50, 52, 67, 69) by pressure water of the temperature 170 to 200 °C at the ratio water to dry matter 0.5 to 1:1, from the mixture obtained excessive water is removed by pressing (51) to the ratio of dry matter to water 1:0.3 to 0.5, consequently with simultaneous feed of pressure water of the temperature 170 to 200 °C in the ratio to dry matter 1:2.5 to 4 it is hydrolysed at the temperature 160 to 230 °C and pressure 0.6 to 2.8 MPa for 3 to 18 minutes, while hydrolysis proceeds with simultaneous uniform advancement (54) of solid and liquid phases, after termination of hydrolysis the material is expanded in two stages (56, 57) giving rise to gaseous phase (2, 3) and hydrolysate (62), gaseous phase contains furfural, methanol and acetic acid, hydrolysate contains cellulose, lignin and water, gaseous phase is rectified (59) and separated to furfural (7) mixture and mixture of acetic acid, formic acid and water (8), water is removed from hydrolysate by pressing (64) and solid remnant (11) is extracted (66) by solvent from group formed by ethanol or acetone, lignin is extracted to the solvent and after evaporation of the solvent reactive lignin is obtained, cellulose remains in solid phase, furfural obtained from the gaseous phase is purified by other distillation and pure furfural may be further treated to furane.</p>			

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1 Method of processing of lignocellulose materials by continuous pressure hydrolysis and corresponding equipment.

The field of technology

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The invention concerns the method of processing of lignocellulose materials by continuous pressure hydrolysis giving rise to lignin, furfural or furane, furfuralalcohol, acetic and formic acid, cellulose or 10 glucose and 10 corresponding equipment for performance of this method.

Current state in the field of technology

15 Hydrolysis of lignocellulose materials was carried out 15 by sulphuric acid, later utilisation of sulphurous acid was tested. More modern percolation procedure of hydrolysis was elaborated by Scholler, who used equipment, where vapour, containing sulphuric acid, 20 passed through raw material to be hydrolysed. Countercurrent hydrolysis 20 of moist raw material by 37 % hydrochloric acid or by gaseous hydrogen chloride is known.

Enzymatic method of hydrolysis was also tested. But 25 on industrial scale only hydrolysis by diluted sulphuric acid in percolation reactor is utilised.

Continuous method of hydrolysis of lignocellulose materials has not been utilised on industrial scale. In operational conditions it is difficult to keep short 30 reaction times, to assure quick heating of the mixture and even to assure regeneration of heat, when the process 30 has to be economically sustainable.

Also filtration equipment, on which continuous operation of the whole equipment depends, represents 35 great problem. Non-hydrolysed fractions may form suspensions with poor filtrability.

Some procedures use multistage hydrolysis utilising

1 hydrochloric acid of different concentrations.

Further on we give short review of hydrolytic and dehydration procedures.

- Production of furfuralaldehyde by discontinuous hydrolysis of lignocellulose by sulphuric acid (5% water solution) at the temperature 145-170 °C.

- Similar system of production of furfuralaldehyde from leafy wood. Chips are mixed with acid in worm type apparatus.

10 - Water extract of superphosphate (containing 45% of P2O5), which is added directly into the autoclave is utilised in catalytic dehydration in the production of furane from furfuralaldehyde.

15 - Continuous hydrolysis is known, using single stage expansion only and raw material is impregnated by sulphuric acid before hydrolysis.

Common shortage of all above mentioned procedure of obtaining of furfural and other components is low yield of the final product, which in operational conditions 20 does not exceed 30 to 45 % of the theoretical value and insufficient utilisation of some components of raw materials used.

When using fluid procedure decrease in yields is caused also by thermooxidising decomposition of 25 furfuralaldehyde in reaction with air oxygen. Oxygen flows into the reaction space in chamber method during dosing.

30 Patents and laboratory systems of the Stake Technology company, Forintek consider prehydrolysis of cellulose and consequently with cellulose hydrolysis. Prehydrolysis does not fulfil its expected function of hemicellulose decomposition and transition to so called pure fraction, to the second stage of lignin and cellulose. In the second phase of cellulose hydrolysis 35 remnants of cellulose exist in range, causing inhibition of consequent fermentation procedures.

Current known methods of hydrolysis of

1 lignocellulose materials are demanding from the point of view of energy consumption, do not cover complex effective and optimal separation of products arising in hydrolysis or at low energy consumption give rise to
5 high costs of regeneration of acids.

The substance of the invention.

Above mentioned disadvantages of given methods of hydrolysis procedures of production of furfural, or furane eventually, cellulose or glucose eventually and pure lignin are solved and removed by the method of continuous pressure hydrolysis of lignocellulose materials, in presence of inorganic acid if need be,
10 with subsequent expansion and separation of hydrolysate and gaseous phase, according the invention. The substance of the invention consists mainly in moisturising of disintegrated raw material at pressure and heating it by pressure water of temperature 170 to
15 200 °C at the ratio of water to dry substance 0.5 to 1:1. For the mixture obtained excessive water is pressed off to the ratio of water to dry matter 1:0.3 to 0.5. Consequently with simultaneous feeding of pressure water at the temperature 170 to 200 °C at the ratio to dry
20 matter 1:2.5 to 4 mixture is hydrolysed at the temperature 160 to 230 °C and pressure 0.6 to 2.8 MPa for the period of 3 to 18 minutes, while hydrolysis proceeds with simultaneous steady process of solid and gaseous phases. After termination of hydrolysis the
25 material is expanded in two stages giving rise to gaseous phase and hydrolysate. Gaseous phase contains furfural, methanol and lower organic acids, hydrolysate contains cellulose, lignin and water. Gaseous phase is rectified and it is separated to furfural mixture and
30 mixture of acetic acid, formic acid and water. Water is removed from the hydrolysate by pressing and solid remnant is extracted for 10 to 35 minutes by the solvent
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1 formed by ethanol or acetone. Lignin is transferred to the solvent, cellulose remains in the solid phase.

5 Simultaneously with the feed of pressure water to the hydrolysis process at the ratio to dry substance 1:2.5 to 4 it is possible to dose sulphuric acid at the amount 0.1 to 0.3 % of the mass of sulphuric acid in respect to the mass of suspension, after hydrolysis the hydrolysate obtained, containing sugars and lignin and fraction of non-hydrolysed cellulose and water are 10 pressed, solution containing sugars is separated and the solid remnant is further on treated by extraction or it returns back to hydrolysis. Solution containing sugar may be processed further by fermentation method to ethanol.

15 Furfural mixture is distilled and pure furfural is treated by sodium hydroxide. Arising salt of furoic acid is melted at the temperature 200 to 240 °C to furane or catalysts at the temperature 350 to 430 °C act on furane.

20 The first expansion proceeds with advantage at the temperature 130 to 170 °C and the pressure 0.25 to 0.9 MPa and the second expansion proceeds at the temperature 105 to 120 °C and the pressure 0.12 to 0.2 MPa.

25 Overall heating of raw materials is provided by pressure water and preheating of all recirculated non-hydrolysed material is provided by expansion steam and after that directly by the pressure water.

30 The equipment consists of the reservoir of raw material, which is via feeding press of worm type and insert connected with the first section of the hydrolyser, where worm conveyor is situated. Output from the last section of the hydrolyser is equipped by high-pressure expansion slide valve, which is followed by middle-pressure expander and low-pressure expander. 35 In the upper part of the expanders the second and third tubing for outlet of the gaseous phase are located, the second tubing for outlet from the middle pressure

1 expander is directed to the system of recuperation exchangers with its mouth in the upper part of the rectification column. In the upper part of the column exhaust of furfural and methanol and in the bottom part 5 exhaust of the mixture of formic acid, acetic acid and water are located. The third tubing for outlet of the vapour phase from the low-pressure expander may pass through the lower part of the rectification column and it leads in the middle part of the rectification column.

10 The lower part of the middle-pressure expander is connected via middle-pressure slide valve with the first tubing for hydrolysate and solid phase with the low-pressure expander. This expander is connected via low-pressure expansion slide valve by the fourth tubing 15 for hydrolysate and solid phase with the reservoir for hydrolysate and solid phase, from which outlet of vapours is directed to the rectification column. The reservoir for hydrolysate and solid phase is via pump connected with the separation equipment. The separation 20 equipment is provided by the fifth tubing for outlet of the liquid hydrolysate to the reservoir of hydrolysate and by conveyor for output of the solid phase after hydrolysis, which is connected to extractor and reservoir of the raw material.

25 Filling press consists of the cylindrical part and conical part. A worm with constant lead in the cylindrical part and with decreasing lead in the conical part goes through both parts of the press, while the conical part consists of segments, among which are gaps 30 for outlet of the liquid to the reservoir of liquid, the conical part is provided inside by longitudinal guide bars, the front face of the cylindrical part is perforated.

The insert is tightly connected with the filling 35 press and it leads to the first section of the hydrolyser and it consists of input conical narrowing part, cylindrical part and conical widening part.

1 Opposite the outlet of the conical widening part safety closing piston, controlled by adjustable pressure is situated.

The expanders have the form of cyclone separators 5 and the outlet of hydrolyser enters tangentially the middle-pressure expander and the first tubing 10 for hydrolysate and solid phase enters tangentially the low-pressure expander. The second and third tubes for outlet of the vapour phase from expanders are recessed 10 to the upper parts of expander below the level of the mouth of the outlet from the hydrolyser and the first tubing for hydrolysate and solid phase. In the bottom part of the middle-pressure expander middle-pressure expansion slide valve is situated and in the bottom part 15 of the low-pressure expander low-pressure expansion slide valve is situated.

The hydrolyser consists of at least one section, sections are connected by vertical tube or by widening cone. All sections are provided by exhaust of inert 20 gases and worm conveyor passes through all sections.

In the reservoir for raw material the material is preheated to the temperature of 85 to 90 °C by feed of small amount of technological pressure water of the temperature 170 to 200 °C, which acts thanks to its 25 expansion very intensively on the material. Moistened preheated material is relieved of excessive moisture in the conical part of the filling press, which is equipped by effective dewatering system, which reliably removes the excessive liquid, which represents great problem for 30 most current equipment. The filling press presses material into the insert, in which it forms compact plug. Its purpose is to separate atmospheric medium of the filling press from the high-pressure medium in the hydrolyser. In this model the insert is in addition in 35 contrast to all known solutions provided by conical widening part, which substantially improves the main function of the plug, i.e. safe separation of the

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1 pressure chamber in the hydrolyser from the
surroundings. In the hydrolyser the material is mixed
with pressure water in the ratio of dry matter to water
1:2.5 to 1:4. Water may contain sulphuric acid in the
5 amount of 0.1 to 0.3 % mass related to the suspension
mass. Concentrated sulphuric acid is mixed with water to
the concentration 0.2 to 0.4% mass, before feeding into
10 the hydrolyser in such way, that into the hydrolyser
added. Mixture of water and material moves on through
the equipment due to rotation of worm conveyor and
15 hydrolyser inert gases are continuously removed through
substantially by plug flow. From the upper part of the
hydrolyser through the last section the decomposed material is
squeezed out into high-pressure expansion slide valve.
20 from which the expanded mixture is displaced into the
middle pressure-expander, where the temperature is in
the range 130 to 175 °C and pressure is in the range
0.25 to 0.9 MPa. Here expander in the form of cyclone
25 separator is utilised with great advantage. The material
is brought in tangentially to the cylindrical part. The
hydrolysate and solid phase expand further in the
low-pressure expander to the temperature 105 to 120 °C
and pressure 0.12 to 0.20 MPa. Expander functions on the
30 same principle of the cyclone separator. The last vapour
fraction is released from the reservoir of hydrolysate and solid phase.
35 reservoir is pumped together with the hydrolysate in the
separators, where solid phase is separated, which
consists of lignin and cellulose. Due to the rotation flow perfect separation
of the solid phase and hydrolysate from the vapour phase
occurs. The hydrolysate contains 0.1 mass% of furfural
at maximum and in the same time faultless outlet of the

1 solid phase from expander is guaranteed.

The main advantage of the equipment is high energetic efficiency, which is enabled by double expansion. Vapour leaves the middle-pressure expander at the temperature 5 130 to 170 °C. This vapour is used in the system of recuperation exchangers for preheating of fresh technologic water to the temperature 125 to 165 °C, so the pressure boiler gives heat only for heating to the temperature of hydrolysis. Other substantial saving of 10 heat results from usage of vapour in the low-pressure expander for heating in the boiler of the rectification column. Double expansion has also the advantage of perfect exhaust of furfural from hydrolysed solution, where its presence is undesirable due to consequent 15 fermentation. The vapour phase from expanders is separated in the rectification column to furfural and methanol and to water solution of inorganic acids. Furfural may be further purified in distillation column, it is obtained in high purity and yielding, 60% related 20 to original pentosanes in the hydrolysed material. Furfural maybe processed further to furane.

Low consumption of water belongs among other advantages of this method and equipment. It is due to the fact, that all recycled water and recycled 25 hydrolysate are heated to temperature needed for hydrolysis in the system of recuperation exchangers and by direct heating by pressure water: in this way problem of encrustation of sugars on the walls at high temperatures is eliminated.

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The advantage of the method and equipment according to the invention is, that the production process is:

- continuous
- 35 - single staged
- the equipment is capable to process wide range of types of input raw materials

- 1 - continuous exhaust of inert gases
- hydrolysate containing sugar does not contain inhibitors of fermentation processes
- 90 to 100% splitting of input lignocellulose
- 5 - shorter time for extraction of lignin than in other currently known procedures
- production of pure products: cellulose, glucose eventually, lignin, furfural, furane, acetic acid, formic acid, methanol, ethanol
- 10 - high yielding of individual products, yielding of furfural is 48 to 60%, of cellulose 95% of input cellulose, of glucose 65% related to input cellulose, of lignin 80 to 90% of input raw material related to wheat straw
- 15 - production of highly reactive lignin
- equipment is provided by fluent dosing of input raw materials
- variability of temperatures in the range from 160 to 230 °C
- 20 - building-block system of main equipment of the line
- optimisation for all types of raw material
- fluent expansion
- safety of the system

25 Review of pictures:

Fig. 1 is the scheme of the whole equipment for hydrolysis.

Fig. 2 shows the filling press 51.

30 Fig. 3 shows the insert 52.

Fig. 4 Shows the scheme of the equipment for production of furane from furfural via furoic acid.

Fig. 5 shows the scheme of the equipment for direct production of furane from furfural.

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Examples of application of the method.

1 The disintegrated straw is moistened and heated by pressure water of temperature 200 °C in the ratio of water to the dry matter 0.8:1 to the temperature of 90 °C. From obtained mixture the excessive water is
5 removed by pressing to the ratio of dry matter to water 1:0.4 and consequently it is hydrolysed at the temperature 200 °C and corresponding pressure for 8 minutes under simultaneous feed of pressure water of the temperature 200 °C in the ratio to the dry matter 1:3.5.
10 The hydrolysis proceeds with uniform steady process of solid and liquid phases. After termination of hydrolysis the material is expanded in two stages giving rise to vapour phase and hydrolysate. The vapour phase contains furfural, methanol and lower organic acids, the
15 hydrolysate contains cellulose, lignin and water. The vapour phase is rectified and separated to furfural mixture and mixture of acetic and formic acids and water. Water is removed from the hydrolysate by pressing and the solid remnant undergoes extraction by acetone
20 for 30 minutes. Into the acetone phase lignin is extracted and after evaporation of the solvent reactive lignin is obtained, cellulose remains in the solid phase.

Wheat straw contained 480 kg of cellulose, 270 kg of
25 pentosanes and 130 kg of lignin related to 1000 kg of dry matter. Using procedure according the invention 456 kg of pure cellulose was obtained, which represents 95 % yielding, 100 kg of furfural, which is 53% yielding and 117 kg of pure lignin, which is 80% yielding.

30 Furfural was further processed to furane. Yielding of furane in respect to furfural was 60% using the direct method, via furoic acid it was 50%.

Example 2

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Using the same procedure as in example 1 maize spindles and beech fillings were processed. In case of

1 maize spindles yielding of cellulose was 85%, of furfural 51% and of lignin 80%. In case of beech fillings yielding of cellulose was 85%, of furfural 50% and of lignin 80%.

5

Example 3

All these raw materials were processed by similar procedure as in example 1 but material, entering 10 hydrolysis was simultaneously wetted by pressure water with 0.2% mass. of sulphuric acid related to the mass of the suspension. The ratio of water to dry matter was 1:4. The first expansion was made at the temperature 160 °C and the second expansion at the temperature 15 105 °C. Hydrolysate obtained after hydrolysis, containing sugar and lignin, and fraction of non-hydrolysed cellulose and water was pressed, solution containing sugar was separated and solid remnant was further treated by extraction. From the sugar containing 20 solution ethanol was produced by fermentation procedure in yield 60% related to glucose.

In case of wheat straw instead of cellulose glucose was obtained in the yield 65% with respect to original content of cellulose in straw, in case of maize spindle 25 and beech fillings it was 57%.

Example 4

Description of equipment on individual figures and 30 its function. The scheme of whole equipment for hydrolysis is shown in figure 1.

The equipment consists of the reservoir 50 of raw material, which is via the filling worm press 51 and the insert 52 connected with the first section of the 35 hydrolyser 53, where the worm conveyer 54 is situated. The filling worm press 51 is connected with the reservoir 67 for liquid removed by pressing. The

1 reservoir 50 of raw materials and hydrolyser 53 are equipped by feed of pressure water from the boiler 69.

The hydrolyser 53 consists of three sections, sections are connected by vertical tube or by widening 5 cone. Outlet from the last section of the hydrolyser 53 is equipped by the worm equipment 68 and the high-pressure expansion slide valve 55, which is followed by the middle-pressure expander 56, which followed by the low-pressure expander 57. All sections 10 of the hydrolyser 53 are provided with the exhaust 6 of inert gases.

The expanders 56 and 57 have the form of cyclone separators and the outlet 9 from the hydrolyser 53 enters tangentially into the middle-pressure expander 15 56. The first tubing 1 for hydrolysate and solid phase enters tangentially the low-pressure expander 57. The second tube 2 and third tube 3 for outlet of vapour phase from the expanders 56 and 57 are embedded in to the upper parts of expanders 56 and 57 under the level 20 of the mouth of the output 9 from the hydrolyser 53 and the first tubing 1 for hydrolysate and solid phase. In the bottom part of the middle-pressure expander 56 middle-pressure expansion slide valve 60 is situated and in the bottom part of the low-pressure expander 57 25 low-pressure expansion slide valve 61 is situated.

The second tubing 2 for outlet of the vapour phase from the middle-pressure expander 56 is directed to the system of recuperation exchangers 58 and it is connected with the upper part of the rectification column 59, in 30 the upper part of which the outlet 7 of furfural and methanol is situated and in the bottom part the outlet 8 of mixture of acetic acid, formic acid and water is situated. The third tubing 3 for outlet of the vapour phase from the low pressure expander 57 goes through the 35 bottom part of the rectification column 59 and has its mouth in the middle part of the rectification column 59. The bottom part of the middle-pressure expander 56

1 is connected via middle-pressure expansion slide valve 60 by the first tubing 1 for hydrolysate and solid phase with the low-pressure expander 57. Expander 57 is connected via low-pressure expansion slide valve 61 by 5 the forth tubing 4 for hydrolysate and solid phase by the reservoir 62 for hydrolysate and solid phase which is via the pump 63 connected with the separation equipment 64. Separation equipment 64 is provided by the fifth tubing 5 for outlet of liquid hydrolysate to the 10 reservoir 65 and by the conveyor 11 for outlet of the solid phase after hydrolysis, which is connected with the extractor 66 or with the reservoir 50 for the raw material.

Exhaust 7 of furfural and methanol is connected with 15 the purification block of furfural.

Figure 2 shows the filling press 51, which consists of the cylindrical part 31 and conical part 32. The worm 33 with constant lead in the cylindrical part 31 and 20 with decreasing lead in the conical part 32 passes through both parts, while the conical part 32 consists of segments 34 among which there are gaps 35 for outlet of liquid into the reservoir 67 for liquid removed by press, the conical part 32 is inside equipped by 25 longitudinal guide bars 36, the front face 37 of the cylindrical parts 31 is perforated.

The insert 52 is shown in the figure 3. It is tightly connected with the filling press 51 and it leads 30 into the first section of the hydrolyser 53. It consists of inlet conical narrowing part 38, the cylindrical part 39 and the conical widening part 40. Opposite to the outlet of the conical widening part 40 the safety closing piston 41, controlled by adjustable pressure is 35 located.

The scheme of equipment for production of furane

1 from furfural via furoic acid is shown in figure 4.

The equipment consists of the furfural reservoir 71 which is via the first exchanger 72 connected with the first vessel 73, which is connected with the reservoir 75 of sodium hydroxide and with the second vessel 76, which is followed by the third vessel 77. All 3 vessels are equipped by stirrers and cooling. The third vessel 77 is connected with extraction column 74, which is connected with the forth vessel 80 for removal of water from ether extract, which is connected with the reservoir 79 of magnesium sulphate and with the first drum filter 81.

Filter is followed by the conveyer 82 and by the annealing furnace 83 for magnesium sulphate. The annealing furnace is via the second exchanger 84 connected with the ether reservoir 78 and with the reservoir 79 of magnesium sulphate.

The first drum filter 81 is connected via the reservoir 85 of semi-product with the distillation column 86. The upper plate of the column 86 is connected with the reservoir 78 of ether and bottom plates are connected with the reservoir 87 of 2-furfuralalcohol. The bottom part of the extraction column 74 is connected via the fifth vessel 88 with the crystallisator 90, which is provided by cooling. The crystallisator 90 is connected to the sixth vessel 91, which is connected via the conveyor 92 with the reservoir 93 of activated carbon, the sixth vessel 91 is via the second drum filter 94 and the third exchanger 95 and other third drum filter 96 connected with the reservoir 97 of furoic acid. This reservoir is via the third conveyor 98 connected with the melting furnace 99, which is followed by the reservoir 100 of furane.

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Fig. 5 shows the scheme of direct production of furane from furfural, which consists of reservoir of

1 furfural 71, which is followed by the pressure melting
furnace 101, which is via the exchanger 102 connected
with the reservoir of furane 103. The pressure melting
furnace 101 is further connected with burning chamber
5 104.

Vegetable raw material is dosed via continuous
balance to the reservoir of raw material 50, from which
it is swept out by worm 52 to the filling press 51,
10 where in the front cylindrical part 31 it is preheated
by pressure water or steam to about 90 °C. The filling
press 51 presses the material via narrowed insert 52
into the hydrolyser 53. Liquid removed by pressing in
the filling press 51 flows to the reservoir 67 of the
15 removed liquid, from which it is pumped back to the feed
of the filling press 51. In the insert 52 compact plug
is formed, which separates the hydrolyser from the view
of pressure. Compactness and impermeability of the plug
is assured by the safety piston 41. Material entering
20 the first section of the hydrolyser 53 is wetted from
above by pressure water of the temperature 170 to
200 °C, eventually by sulphuric acid, in case when
decomposition of cellulose is the purpose. Material is
uniformly moved forward by the worm conveyor 54 with
25 liquid in the hydrolyser 53 at the temperature 160 to
230 °C at the pressure 0.6 to 2.8 Mpa.

The whole time of retention (delay) of material and
liquid is the same, i.e. from 3 to 12 minutes. At the
end of the section material with the liquid falls into
30 the next section of the hydrolyser 53. All sections of
the hydrolyser 53 work at the same pressure. From the
upper part inert gases are removed continuously by the
exhaust 6. From the last section of the hydrolyser 53
35 material and liquid are swept out by the worm equipment
68 into the high-pressure slide valve 55, behind which
the mixture is expanded to middle pressure 0.25 to 0.9
MPa and temperature from 130 to 175 °C. In the

1 middle-pressure expander 56 vapor phase is separated.
Its heat content is utilised in the system of
recuperation exchangers 58 for pre-heating of
technological water. The condensed vapour phase is
5 brought into the rectification column 59. Liquid and
solid phases from the middle-pressure expander 56 are
directed via middle-pressure expansion slide valve 60 to
the low-pressure expander 57, in which the temperature
is in the range 105 to 120 °C and pressure 0.12 to 0.2
10 MPa. The released vapour is used for heating in the
boiler of the rectification column 59. Liquid and solid
phase is removed via low-pressure expansion slide valve
61 to the reservoir 62 for hydrolysate and solid phase.
From this reservoir released vapour phase is also
15 directed into the rectification column 59. Liquid and solid
phases proceed into the separator 64, where they
are separated to solid phase, which consists mostly of
lignin and non-reacted cellulose. Both substance are
separated in the extractor 66.

20 Liquid hydrolysate with monosacharides is removed in
case of acidic hydrolysis via the reservoir 65 for
further treatment e.g. for fermentation. Liquid
hydrolysate contains in case of acidic hydrolysis 12 to
15% mass. of glucose and it is further processed e.g. to
25 ethanol.

In case of acidic hydrolysis part of solid phase,
which has not reacted and contains first of all
cellulose, is recycled and it forms feed to the
hydrolyser 53. In case when the hydrolysis is carried
30 out only by steam, liquid hydrolysate is pre-heated in
the system of recuperation exchanger 58 and it is
returned to the hydrolyser 53. What is substantial, is,
that no recirculated solution does not pass through the
pressure boiler 69, but it is heated to the necessary
35 temperature by pressure water, produced by heating of
fresh technological water in the pressure boiler 69.

In the head of the rectification column 59 exhaust

1 7 of furfural and methanol is situated. In the bottom part exhaust 8 of mixture of acetic acid, formic acid and water is situated.

5 Furfural fraction is further purified by distillation and it is collected in the reservoir 71 of furfural.

From the reservoir of furfural 71 in figure 4 furfural cooled in the first exchanger 72 to temperature 5 to 8 °C is pumped to the first vessel 73. Into this 10 vessel sodium hydroxide is dosed from the reservoir 75. Salt of furoic acid and 2-furfuralalcohol are formed by reaction with hydroxide. The time of delay of mixture in the first vessel 73 is about 20 minutes. The temperature may not exceed 20 °C. Mixture is then moved due to 15 self-slant to the second stirred vessel 76, where the reaction terminates. Time of delay in the second vessel 76 is about 60 minutes. Also this second vessel 76 has to be intensively cooled. Mixture is moved by self-slant to the third vessel 77, which is also cooled. 20 Due to cooling crystals of the salt of furoic acid are separated out and they form precipitate, which is eliminated by addition of water. From this vessel mixture is moved by pumping to the extraction column 74, where continuous extraction of 2-furfuralalcohol by 25 ether occurs. Ether is pumped from the reservoir 78.

Water is removed from the extracted 2-furfuralalcohol with ether and casual impurities by addition of dehydrated magnesium sulphate MgSO₄, which is stored in the reservoir 79 of magnesium sulphate. 30 Mixing is carried out in the fourth vessel 80. Magnesium sulphate absorbs water and creates hydrate MgSO₄.7H₂O, which crystallises. These crystals are removed in the first drum filter 81 and they are transported by the first conveyor 82 into the annealing furnace 83, where 35 sulphate is regenerated. The furnace 83 is blown through by air and ether vapours are removed, which are further on condensed in the second exchanger 84 and return to

1 the ether reservoir 78. Water from hydrate MgSO₄ is then
removed by roasting, regenerated magnesium sulphate is
returned by conveyor to the reservoir 79.

5 Filtrate from the first drum filter 81 is removed
to the reservoir of semi-product 85. This mixture
contains only 2-furfuralalcohol and ether, impurities
(water, magnesium sulphate, furoic acid) eventually.
This mixture is pumped into vacuum distillation column
86. From the upper plate ether is removed, which is
10 directed back to the reservoir 78 and from the bottom
plate 2-furfuralalcohol is removed, which is stored in
the 2-furfuralalcohol reservoir 87.

The second steam, leaving the extraction column
74, contains sodium salt of furoic acid. Conversion to
15 furoic acid proceeds by acidification in the fifth
vessel 88. By cooling in the crystalliser 90 crystals of
furoic acid are precipitated and sodium hydrogensulphate
(according to pH precipitation of sulphate may occur).
After separation of these two substances it is necessary
20 at first to suck away excessive water. This is done in
the crystalliser 90. Then the mixture is boiled with
activated carbon in the sixth vessel 91. Activated
carbon is dosed by the second conveyor of activated
carbon 92 from the reservoir of activated carbon 93.
25 Boiling lasts for about 45 minutes. Activated carbon is
then removed from the mixture on the second filter 94
and is regenerated in simple way by blowing-through by
air in the reservoir of activated carbon 93.

Filtrate is transported by pump via the fourth
30 exchanger 95 to the third drum filter 96. In the fourth
exchanger 95 the mixture is cooled to the temperature
16 to 20 °C (below the temperature 10 °C even the rest
of hydrogen sulphate is separated out and above the
temperature 20 °C crystallisation is not sufficiently
35 intensive). Crystals separated out are then removed on
the third filter 96. Filtrate, containing water solution
of hydrogensulphate, or sulphate respectively, leaves

1 for the sodium sulphate reservoir. Crystals of furoic acid are stored in the reservoir of furoic acid 97 and from there they are dosed by the third conveyor 98 to the furnace 99, where melting of the acid at the 5 temperature 230 °C occurs. In this process carbon dioxide is intensively separated out, which is separated after cooling of furane. Due to high volatility it is necessary to keep furane at low temperature and in closed vessel 100.

10 From the reservoir 71 (fig.5) furfural is dosed to the pressure melting furnace 101, where catalyst (CaO, CaCO₃, MnCrO₂ or ZnCrO₂) is added. After closure the pressure melting furnace 101 is heated to the temperature 400 °C. Furane is separated out and it is 15 cooled and stored in the furane reservoir 103. Considerable amount of carbon oxide also leaves the pressure melting furnace 101. It is necessary to destroy it safely by burning in the burning chamber 104. This production process cannot be carried out continuously 20 because of high temperature and pressure, at which the reaction in pressure melting furnace 101 occurs.

Industrial application

25 The invention may be utilised for complex and effective processing of sources of phytomass sources as new perspective sources of non-fossil raw materials in the tight bond to chemical, pharmaceutical and food industries.

1

Patent claims

1. The method of processing of lignocellulose materials by continuous pressure hydrolysis, or in the presence of inorganic acid respectively, by consequent expansion and separation of the hydrolysate and gaseous phase, characterised by the fact, that disintegrated raw material is wetted and heated by pressure water of the 10 temperature 170 to 200 °C at the ratio water to dry matter 0.5 to 1:1, from the mixture obtained excessive water is removed by pressing to the ratio of dry matter to water 1:0.3 to 0.5, consequently with simultaneous feed of pressure water of the temperature 170 to 200 °C 15 in the ratio to dry matter 1:2.5 to 4 it is hydrolysed at the temperature 160 to 230 °C and pressure 0.6 to 2.8 MPa for 3 to 18 minutes, while hydrolysis proceeds with simultaneous uniform advancement of solid and liquid phases, after termination of hydrolysis the 20 material is expanded in two stages giving rise to gaseous phase and hydrolysate, gaseous phase contains furfural, methanol and acetic acid, hydrolysate contains cellulose, lignin and water, gaseous phase is rectified and separated to furfural mixture and mixture of acetic 25 acid, formic acid and water, water is removed from hydrolysate by pressing and solid remnant is extracted by solvent from group formed by ethanol or acetone, lignin is extracted to the solvent and after evaporation of the solvent reactive lignin is obtained, cellulose 30 remains in solid phase, furfural obtained from the gaseous phase is purified by other distillation and pure furfural may be further treated to furane.

2. The method according to claim 1, characterised by 35 the fact, that together with the feed of pressure water into the process of hydrolysis at the ratio to dry matter 1:2.5 to 4 sulphuric acid is dosed in the amount

1 of 0.1 to 0.3 mass % of sulphuric acid, in respect to
suspension mass, after hydrolysis the hydrolysate
obtained containing sugars and lignin, non-hydrolysed
5 cellulose and water is pressed, solution containing
sugars is separated and solid remnant is further treated
by extraction or it is returned to hydrolysis, solution
containing sugars may be without sterilisation further
processed by fermentation method to ethanol.

10 3. The method according the claims 1 and 2,
characterised by the fact, that the first expansion
proceeds at the temperature 130 to 175 °C and the
pressure 0.25 to 0.9 MPa and the second expansion
proceeds at the temperature 105 to 120 °C and pressure
15 0.12 to 0.2 MPa.

4. The method according the claims 1 and 3,
characterised by the fact, that all heating of raw
materials is carried out directly by pressure water and
20 pre-heating of all recirculated non-hydrolysed material
is made by expansion steam and after that directly by
pressure water.

5. The method according the claims 1 and 4,
25 characterised by the fact, that furfural is affected by
a catalyst from the group CaO, CaCO₃, MnCrO₂ or ZnCrO₂
at the temperature 400 °C giving rise to furane.

6. The method according the claims 1 and 4, charac-
30 terised by the fact, that cooled pure furfural is mixed
with sodium hydroxide giving rise to salt of furoic acid
(2-furfuralcarboxylic acid) and 2-furfuralalcohol, the
mixture is cooled to maximal temperature 20 °C, by addi-
35 tion of water crystals of separated out salt of furoic
acid are eliminated, 2-furfuralalcohol is extracted by
ether, solution containing ether is deprived of water by
addition of magnesium sulphate, sodium salt of furoic

1 acid is purified by recrystallisation and by activated
carbon and it is melted at 230 °C to furane.

7. The equipment for performance of the method
5 according to the claims 1 and 4, characterised by the
fact, that it consists of the reservoir of raw material
(50), which is connected via filling press (51) and the
insert (52) with the first section of the hydrolyser
(53), where the worm conveyer (54) is situated, and it
10 is equipped by exhaust of inert gases (6), outlet of the
last section of the hydrolyser (53) is equipped by high-
pressure expansion slide valve (55) and it is followed
by middle pressure expander (56) and it is followed by
low-pressure expander (57), in the upper parts of the
15 expanders (56 and 57) the second tubing (2) and the
third tubing (3) for outlet of vapour phase are
situated, the second tubing (2) for outlet of vapour
phase from the middle pressure expander (56) passes
through the system of recuperation exchangers (58) and
20 it has its mouth in the upper part of the rectification
column (59), in the upper part of which exhaust (7) of
furfural and methanol and in the bottom part exhaust
(8) of mixture of acetic acid, formic acid and water are
situated, the third tubing (3) for outlet of vapour
25 phase from the low-pressure expander (57) leads to the
middle part of the rectification column (59), the bottom
part of the middle pressure expander (56) is connected
via the middle-pressure expansion slide valve (60) with
the first tubing (1) for hydrolysate and solid phase
30 with the low-pressure expander (57) and this expander is
via low-pressure expansion slide valve (61) by the
fourth tubing (4) for hydrolysate and solid phase
connected with the reservoir (62) for hydrolysate and
solid phase, from which the vapour outlet (10) is
35 directed to the rectification column (59), the reservoir
(62) for hydrolysate and solid phase is connected via
pump (63) with the separation equipment (64), the

1 separation equipment (64) is provided by the fifth
tubing (5) for outlet of liquid hydrolysate to the
reservoir (65) of hydrolysate and by the conveyer (11)
for outlet of solid phase after hydrolysis, which is
5 connected to extractor (66) or to the reservoir (50) of
raw material . exhaust (7) of furfural and methanol is
directed to the refining block of furfural.

8. The equipment according to the claim 7,
10 characterised by the fact, that the filling press (51)
consists of the cylindrical part (31) and conical part
(32), the worm (33) with constant lead in the
cylindrical part (31) and with narrowing lead in the
15 conical part (32) goes through both parts, while the
conical part (32) is formed by segments (34) among which
there are gaps (35) for outlet of liquid to the
reservoir (67) of liquid removed by pressing, the
conical part (32) is equipped inside with by
20 longitudinal guide bars (36), front face (37) of the
cylindrical part (31) is perforated.

9. The equipment according to the claims 7 and 8,
characterised by the fact, that the insert (52) is
25 tightly connected with the filling press (51) and it
leads to the first section of the hydrolyser (53) and it
is formed by the input conical narrowing part (38) by
the cylindrical part (39) and by conical widening part
(40). opposite the outlet of the widening part (40) the
safety closing piston (41), controlled by adjustable
30 pressure, is situated.

10. The equipment according to the claims 7 to 9,
characterised by the fact, that the expanders (56 and
57) have form of cyclone separators and the outlet (9)
35 from the hydrolyser (53) enters tangentially the
middle-pressure expander (56) and the first tubing (1)
for hydrolysate and solid phase enters tangentially the

1 low-pressure expander (57), the second tube (2) and the
third tube (3) for outlet of vapour phase from expanders
(56 and 57) are directed to the upper parts of expanders
(56 and 57) below the level of mouth of outlet (9) from
5 the hydrolyser (53) and the first tubing (1) for
hydrolysate and solid phase and in the bottom part of
the middle-pressure expander (56) middle-pressure
expansion slide valve (60) is situated and in the bottom
part of the low-pressure expander (57) low-pressure
10 expansion slide valve (61) is situated.

11. The equipment according to the claims 7 to 10,
characterised by the fact, that the third tubing (3) for
outlet of gaseous phase from the low-pressure expander
15 (57) passes through the bottom part of the rectification
column (59) and after this it leads to its middle part.

12. The equipment according to the claims 7 to 11,
characterised by the fact, that hydrolyser is formed by
20 at least one section, sections are connected by vertical
tube or by widening cone, all sections are provided by
exhaust of inert gases (6) and the worm conveyor (54)
passes through all sections.

25 13. The equipment according to the claims 7 to 12
and for performance of the method according to the claim
5, characterised by the fact, that it consists of the
furfural reservoir (71), which is followed by the
pressure melting furnace (101), which is connected via
30 exchanger (102) with the reservoir of furane (103). The
pressure melting furnace (101) is further connected by
the burning chamber (104).

35 14. The equipment according to the claims 7 to 12
and for performance of the method according to the claim
6, characterised by the fact, that it consists of the
reservoir (71) of furfural which is via the first

1 exchanger (72) connected with the first vessel (73), which is connected with the reservoir (75) of sodium hydroxide and the second vessel (76), which is followed by the third vessel (77), all three vessels are equipped
5 by stirrers and cooling, the third vessel (77) is connected with the extraction column (74), which is connected with the fourth vessel (80) for removal of water from the ether extract, which is connected with the reservoir (79) of magnesium sulphate and with the
10 first filter (81), which is followed by the first conveyor (82) and the annealing furnace (83) of magnesium sulphate, the annealing furnace (83) is via the second exchanger (84) connected with the ether reservoir (78) and with the reservoir (79) of magnesium
15 sulphate, the first filter (81) is connected via the semi-product reservoir (85) with the distillation column (86), the upper plate of the column (86) is connected with the reservoir (78) of ether and the bottom plates are connected with the 2-furfuralalcohol reservoir
20 (87), the bottom part of the extraction column (74) is via the fifth vessel (88) connected with the crystalliser (90), which is provided by cooling, the crystalliser (90) is connected with the sixth vessel (91), which is connected via the second conveyor (92)
25 with the reservoir (93) of activated carbon, the sixth vessel (91) is via the second filter (94) and via the third exchanger (95) and other third filter (96) connected with the reservoir (97) of furoic acid, this reservoir (97) is connected via the third conveyor (98)
30 with the melting furnace (99), which is connected to the furane reservoir (100).

FIG. 1

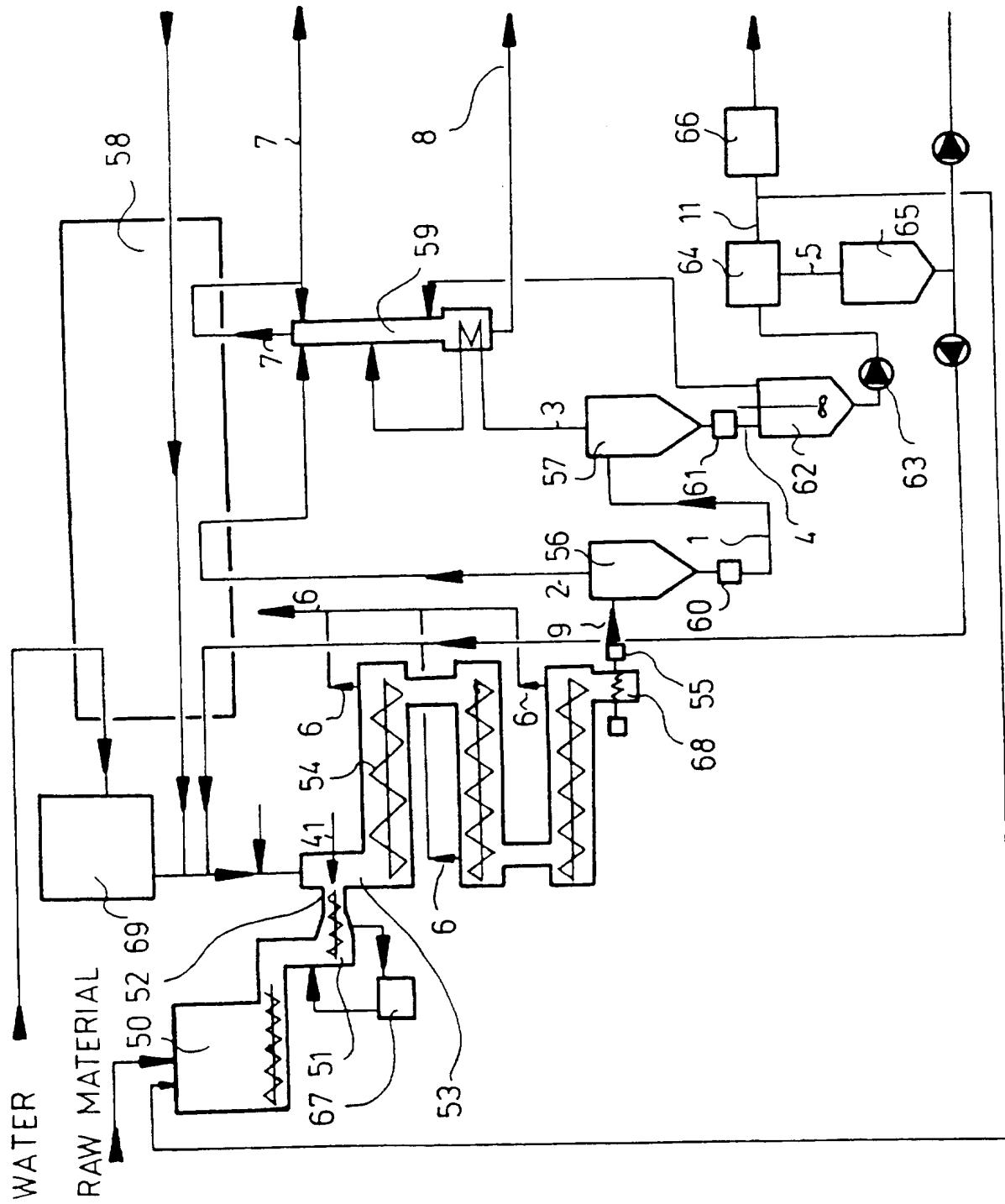


FIG. 2

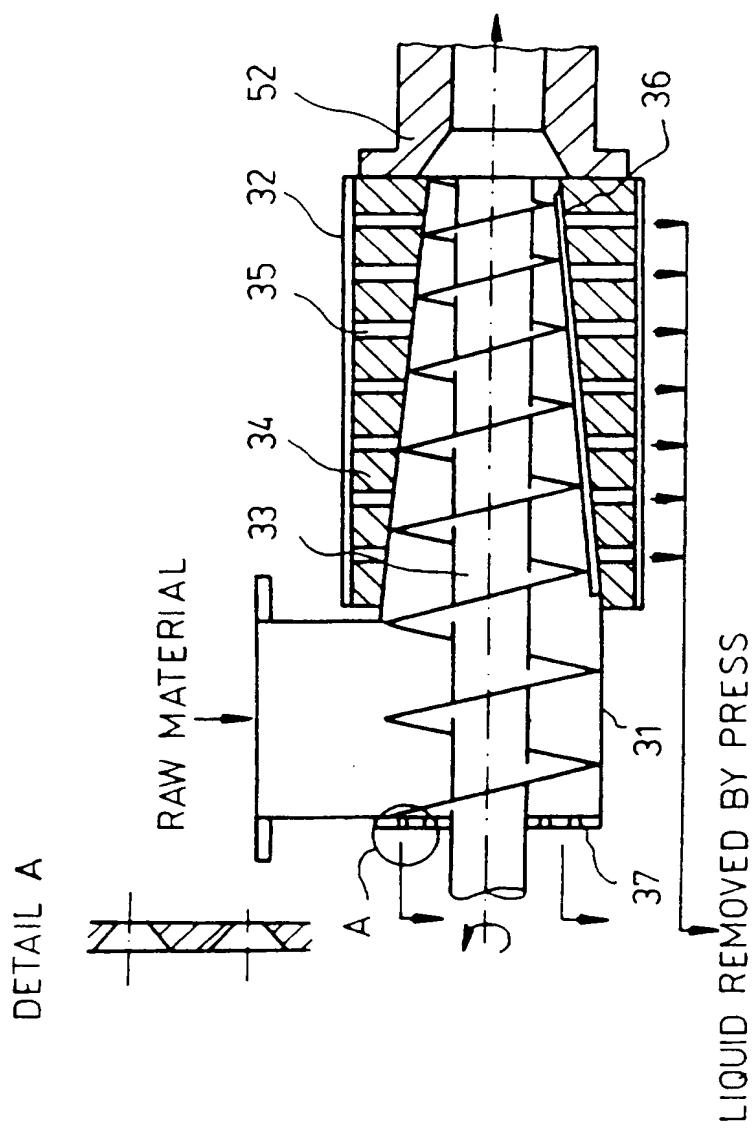


FIG. 3

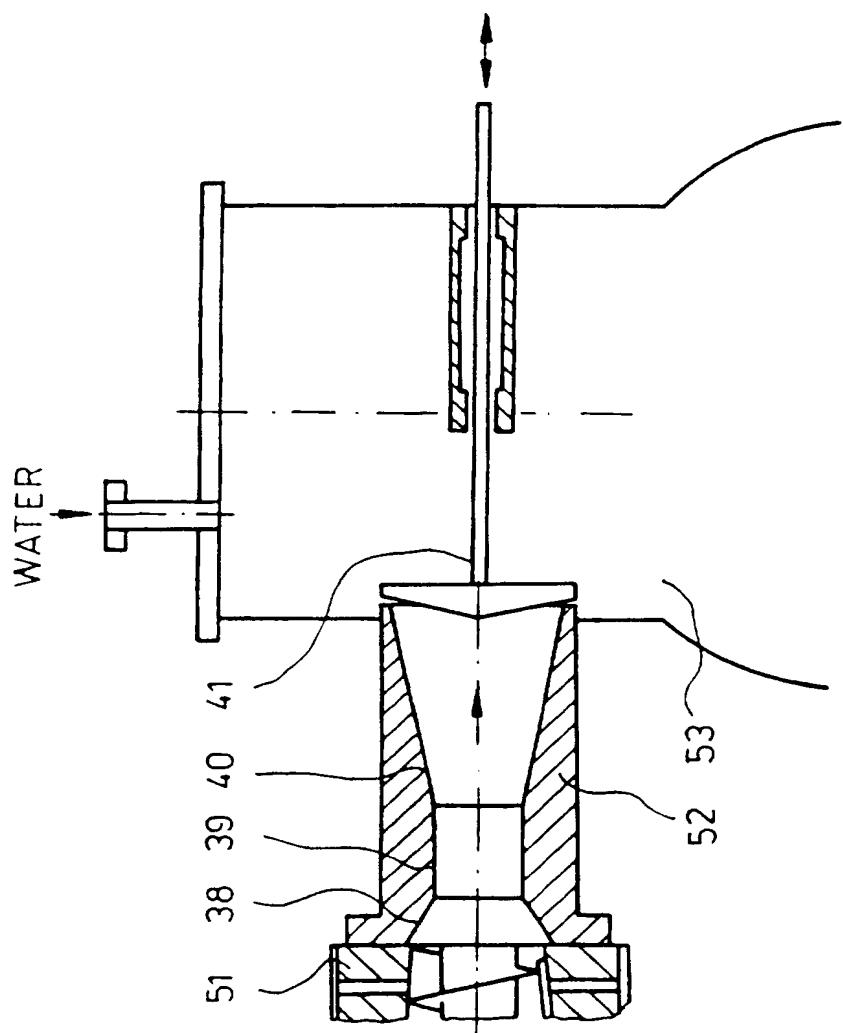


FIG. 4

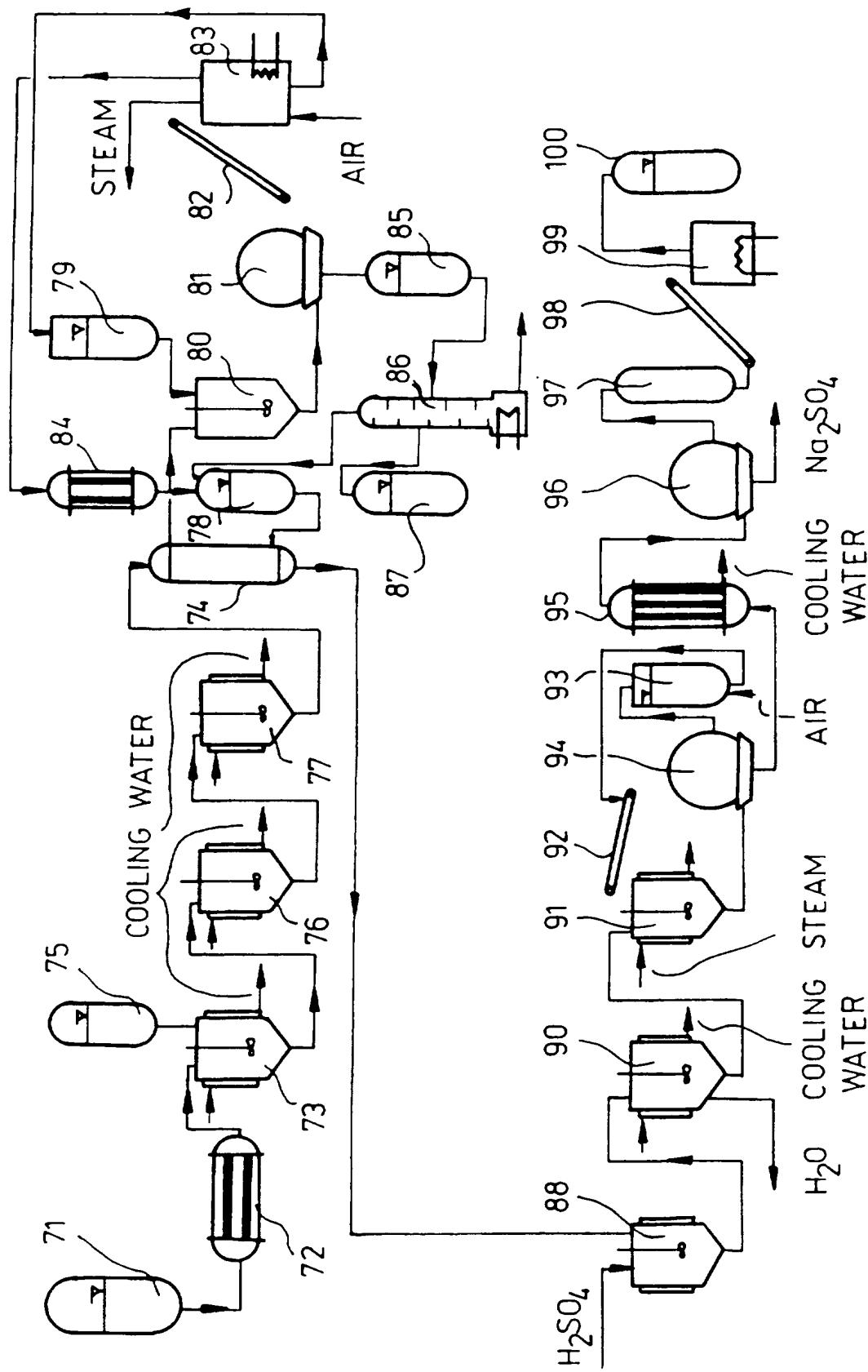
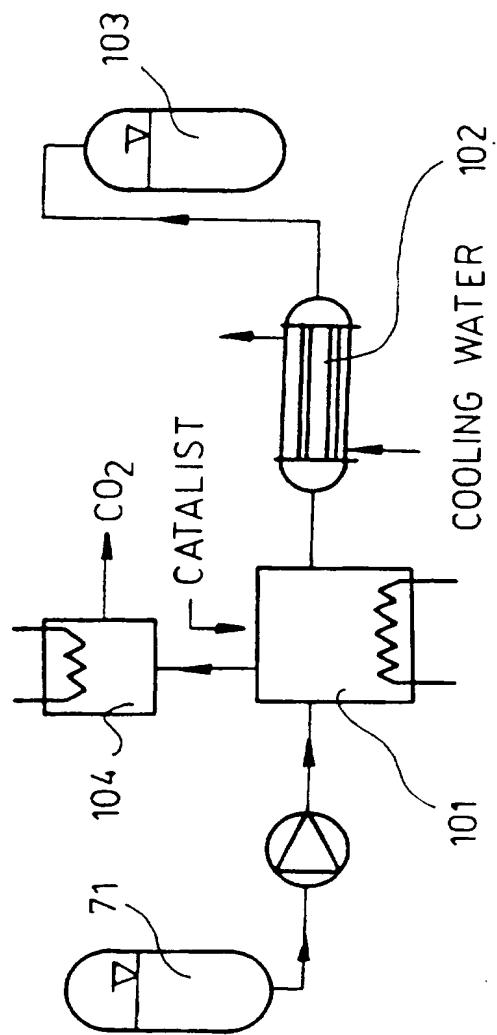


FIG. 5



INTERNATIONAL SEARCH REPORT

International Application No

PCT/CZ 96/00005

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21C11/00 C07D307/50

According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21C C07D

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 291 494 (VOEST ALPINE IND ANLAGEN) 17 November 1988 see column 4, line 13 - column 6, line 24; figure 1 ---	1,2,7
A	EP,A,0 346 836 (JEDNOTNE ZEMEDELSKE DRUZSTVO J) 20 December 1989 see column 7, line 6 - column 11, line 41; figure ---	1,7
A	US,A,4 912 237 (ZEITSCH KARL J) 27 March 1990 see column 8, line 14 - column 10, line 30; figure 1 ---	1,2,7,10
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INTERNATIONAL SEARCH REPORT

International Application No

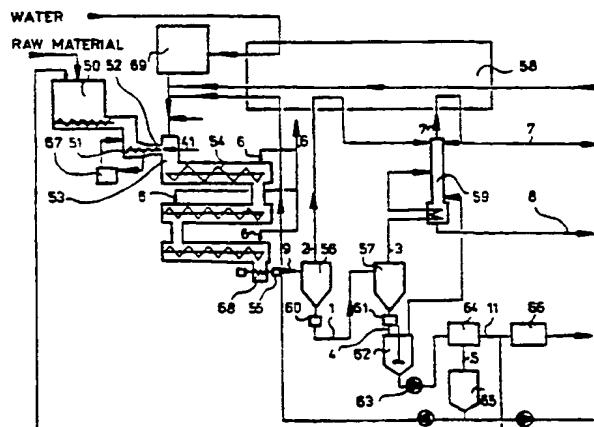
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EP-A-0346836	20-12-89	NONE		
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		CA-A-	1129355	10-08-82
		DE-A-	2944789	24-07-80
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		JP-C-	1168642	30-09-83
		JP-A-	55092699	14-07-80
		JP-B-	57056880	01-12-82
		SE-A-	7903001	13-07-80
US-A-5411594	02-05-95	NONE		

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(74) Agent: KUBÍČKOVÁ, Květoslava; BIC ČVUT Patentové Středisko, Horská 3, 128 03 Praha 2 (CZ).			

(54) Title: METHOD OF PROCESSING OF LIGNOCELLULOSE MATERIALS BY CONTINUOUS PRESSURE HYDROLYSIS AND CORRESPONDING EQUIPMENT



(57) Abstract

The invention relates to a method and an equipment for the processing of lignocellulose materials by one step continuous pressure hydrolysis, optionally in the presence of inorganic acid, by consequent expansion and separation of the hydrolysate and gaseous phase, wherein disintegrated raw material is wetted (50, 52, 67, 69) by pressure water of the temperature 170 to 200 °C at the ratio water to dry matter 0.5 to 1:1, from the mixture obtained excessive water is removed by pressing (51) to the ratio of dry matter to water 1:0.3 to 0.5, consequently with simultaneous feed of pressure water or water with the sulphuric acid in the amount 0.1 to 0.3 mass % of the temperature 170 to 200 °C in the ratio to dry matter 1:2.5 to 4 it is hydrolysed at the temperature 160 to 230 °C and pressure 0.6 to 2.8 MPa for 3 to 18 minutes, while hydrolysis proceeds with simultaneous uniform advancement (54) of solid and liquid phases, after termination of hydrolysis the material is expanded in two stages (56, 57) giving rise to gaseous phase (2, 3) and hydrolysate (62) gaseous phase contains furfural, methanol and acetic acid, hydrolysate contains cellulose, lignin and water, gaseous phase is rectified (59) and separated to furfural (7) mixture and mixture of acetic acid, formic acid and water (8), water is removed from hydrolysate by pressing (64) and solid remnant (11) is extracted (66) by solvent from group formed by ethanol or acetone, lignin is extracted from the solvent and after evaporation of the solvent reactive lignin is obtained, cellulose remains in solid phase, furfural obtained from the gaseous phase is purified by other distillation and pure furfural may be further treated to furane. In case of acidic hydrolysis liquid hydrolysate is formed by glucose.

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